THE USE OF 1,1'-BINAPHTHYL TO STUDY H-DONOR SOLVENTS

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The direct liquefaction of coal uses hydrogen donor solvents which serve a variety of purposes including solvation of coal, shuttling of hydrogens among the different molecules present, and direct hydrogenation of the coal. These processes can be better understood by studying the reactions of each H-donor with the coal or preferably with a model substance whose products are easily analyzed.

One generally accepted mechanism for coal liquefaction involves thermal cleavage to form free radicals which can then either abstract a hydrogen to form a stable lower molecular weight species, rearrange to other molecules, or combine with other free radicals or aromatic molecules to form undesirable high molecular weight polymers (1). The use of hydrogen or synthesis gas (50% hydrogen and 50% carbon monoxide) and tetralin or other H-donor solvents increases yields of distillable product (2).

Some methods developed for studying H-donors involve the generation of benzyl radical by various means and testing the extent that an H-donor will release its hydrogen to the reactive radicals. The generation of benzyl radicals has been carried out with phenylmethyldiazine at 170°C (3), dibenzylmercury at 130-210°C (3), and bibenzyl at 375°C (4); and a scale of reactivity of H-donors with benzyl radical at these temperatures was developed. Attempts were made to correlate results of stabilizing benzyl radical with results of coal-processing experiments.

Benzyl radical systems have several disadvantages. They include the relatively low temperatures compared to liquefaction conditions of the diazine and dibenzyl mercury degradations, and the number of products formed from competing radical reactions.

In an earlier study of the dimerization of phenanthrene (5) we found that the amount of polyphenanthryls and biphenanthryls formed at high temperatures was significantly decreased in the presence of tetralin. At liquefaction temperatures and pressures (460°C and 27.6 MPa), the phenanthryl radical reacted with hydrogen instead of polymerizing. As a model, the phenanthrene system may resemble the coal system. The radicals are stabilized with hydrogen from the H-donor. Analysis problems encountered with the phenanthrene system included formation of a large number of biphenanthryl isomers in a small concentration, the low volatility of biphenanthryls in GC analysis, and the formation of polymers.

A better system of comparing H-donors at coal liquefaction temperatures (450-500°C) was sought which would yield a small number of major products which could be conveniently analyzed by gas chromatography.

DISCUSSION

The stability of a number of biaryls at 470°C was screened. Biaryls tested included 1,1'-binaphthyl, 2,2'-binaphthyl, p-terphenyl, biphenyl, 9,9'-biphenanthryl, and 1,1'-bipyrenyl. They were each heated with tetralin at 470°C for 1 hour. 1,1'-Binaphthyl was observed to form significant yields of the coupling product, perylene.

The coupling of 1,1'-binaphthyl has been reported by Copeland, et al., (6) who found perylene to be formed in 19% yield when heated to 490°C for 3 hours in

the presence of decalin, H_2 gas and catalyst. Gilman and Brennan (7) observed the same product when 1,1'-binaphthyl was placed in dry 1,2-dimethoxyethane and lithium metal. Solodovikov, et al, (8) found perylene to be produced from 1,1'-binaphthyl with potassium in 1,2-dimethoxyethane.

The effect of various hydrogen donors on the dimerization reaction of 1,1'-binaphthyl was studied. Each hydrogen donor (0.5g) was placed in a reaction tube with 1,1'-binaphthyl (0.5g) with benzene (solvent) and heated to 470°C for 1 hour. The results are summarized in Table 1.

TABLE 1

PERYLENE/BINAPHTHYL RATIO FROM REACTION OF H-DONOR
WITH 1,1'-BINAPHTHYL, 1 HOUR AT 470°C

H-Donor	Perylene/Binaphthyl $\times\ 10^2$
1. Blank	1.4
2. Tetralin	1.3
3. Dihydronaphthalene[a]	3.4
4. 9,10-Dihydrophenanthrene	3.1
5. 1,2,3,4-Tetrahydrophenanthrene	7.8
6. Octahydrophenanthrene	6.3
7. 9,10-Dihydroanthracene	17.7
8. Octahydroanthracene	6.3
9. Di and Tetrahydropyrene[b]	14.1
10. 1,2,3,6,7,8-hexahydropyrene	28.0

[a]   Mixture of 72% 1,2- and 28% 1,4-dihydronaphthalene.
[b]   Mixture of 68% 4,5-dihydropyrene and 24% 4,5,9,10-tetrahydropyrene.

In the absence of H-donors, only starting material and rearranged 1,2'-binaphthyl and 2,2'-binaphthyl were observed with packed column GC. When H-donor was added perylene was formed. The reactions had some H-donor and its various dehydrogenated isomers remaining. The binaphthyl and perylene were analyzed by GC and the ratio of perylene/binaphthyl was noted.

The mechanism of coupling is not well understood. Phenanthrene, when reacted in the absence of H-donors, produced products from the phenanthryl radicals formed by thermal cleavage of C-H bonds. The addition of H-donor greatly inhibited but did not completely prevent the formation of these products. The coupling tendencies of the 1,1'-binaphthyl in the presence of H-donors were the reverse of those observed with phenanthryl radical. The coupling of 1,1'-binaphthyl in the 8,8' position is sterically favored, reducing the formation of by-products.

A binaphthyl radical may be formed by thermal cleavage of the C-H bond, but increased amounts of perylene with H-donor suggest that the H-donor is acting as an initiator of the coupling reaction. A mechanism is proposed in Figure 1 which appears to be consistent with the results observed. The proposed mechanism would suggest that more effective hydrogen donors would give higher perylene/binaphthyl ratios.

There appear to be several advantages to this system over phenanthrene or benzyl radical systems of evaluating H-donors. One advantage is the lower molecular weight product compared to the products produced by phenanthrene. Perylene will separate on a 6' x 1/8" 3% Dexsil on 100/200 Supelcoport column in less than 15 minutes with temperatures no higher than 300°C. The biphenanthryls required 30 to 45 minutes and a column temperature programmed to 400°C. Another

advantage of the binaphthyl system is that only one major product (perylene) is produced in the coupling reaction, where several isomers in low yields were found with phenanthryl radicals. A third advantage of the binaphthyl system as a model system to evaluate H-donors as compared to the benzyl system is the substantial decrease in side products. Benzyl radicals react with other radicals and aromatic compounds giving a variety of compounds (9). The close proximity of the proposed free radical at the 8-position of 1,1'-binaphthyl to the 8'-position appears to limit side products from this reaction. Still another advantage of the binaphthyl system over the bibenzyl system is the higher temperature required for coupling of the binaphthyl. The higher temperature more closely resembles liquefaction conditions.

EXPERIMENTAL

1,1'-Binaphthyl, 2,2'-binaphythyl and p-terphenyl were purchased from Eastman Kodak Company. 1,1'-Binaphthyl was also synthesized by established procedures (10).

The hydrogenated H-donors were prepared by reaction of the aromatic hydro-carbons with hydrogen and Na/Rb catalyst (11), with hydrogen and Pd-C catalyst (12), or with Na in amyl alcohol (13). Packed column gas chromatography was used for quantitative analyses and GC-MS was used to identify the components.

Reaction vessels of 2-ml capacity were Gyrolok ½" 316 SS union with end caps. Vessels were heated in a Techne Model SBL-2 fluidized-bed sand bath equipped with a Techne Model TC4D temperature controller which controlled the temperature within 1°C. The time required for heat-up was 5 minutes. Reaction vessels were quenched in water.

ACKNOWLEDGMENT

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Figure 1. Proposed Mechanism for the Formation of Perylene from 1,1'-Binaphthyl with H-Donor